

Electronically Modified Ionic Liquids for Efficient CO₂ Sequestration

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Abstract: A series of imidazole-based ionic liquids (ILs) have been synthesized and examined as potential alternative media for CO₂ sequestration. Several novel ionic liquids have been synthesized with the specific intent of modulating the electronic properties of the imidazole ring. Direct modulation electronics has allowed for faster CO₂ uptake kinetics as well as allowed for lower temperatures to be used in release of the bound CO₂.

Title?

Current Liquid Sorption Processes for CO₂

- Aqueous solutions of amines (i.e. monoethanol amine, diethanolamine)
 - Pros**
 - High Capacity
 - Fast Kinetics
 - Low Initial Cost
 - Cons**
 - Corrosion
 - High Regeneration Cost
 - Volatility

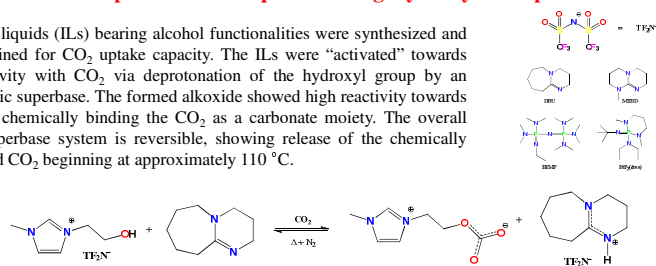
Ionic Liquids as alternative Media for CO₂ Sorption

- Pros**
 - No Vapor Pressure
 - High Thermal Stability
 - Modular Properties
- Cons**
 - Viscosity
 - High Initial Cost

Binding of CO₂ Within Ionic Liquids

Task Specific Ionic Liquids bearing Hydroxyl Groups

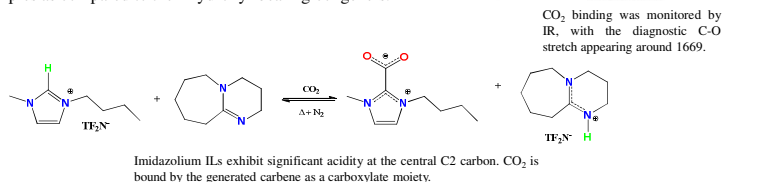
Ionic liquids (ILs) bearing alcohol functionalities were synthesized and examined for CO₂ uptake capacity. The ILs were “activated” towards reactivity with CO₂ via deprotonation of the hydroxyl group by an organic superbase. The formed alkoxide showed high reactivity towards CO₂, chemically binding the CO₂ as a carbonate moiety. The overall IL/superbase system is reversible, showing release of the chemically bound CO₂ beginning at approximately 110 °C.



Deprotonation of the hydroxyl moiety by the organic superbase allows for CO₂ to be bound chemically as a carbonate.

CO₂ Binding Via Deprotonation of Imidazole Ionic Liquids

The central C2 carbon of imidazole rings displays significant acidity, and is capable of being deprotonated via reactions with strong bases. This deprotonation of the central carbon yields an “activated” imidazole ring, which has been shown to bind CO₂ via the C2 carbene. Using this established property, several ILs were reacted with organic superbases and examined for CO₂ binding capabilities. The examined systems not only showed high capacity and reversibility, but afforded less viscous samples as compared to their hydroxyl-bearing congeners.

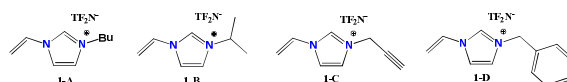


Imidazolium ILs exhibit significant acidity at the central C2 carbon. CO₂ is bound by the generated carbene as a carboxylate moiety.

Electronically Diffuse Ionic Liquids

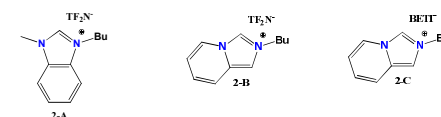
Several ILs were synthesized with the intent of modulating the CO₂ binding properties of imidazole-based ILs. Electron withdrawing groups were tethered to various positions of the imidazole backbone to probe the affect these groups would have on the overall system. In addition to positional affects, withdrawing affects were examined by addition of larger pi-conjugated systems.

N-Vinyl Based Imidazolium Ionic Liquids



N-Vinyl Based ILs synthesized for this study (above). Ancillary alkyl chains were substituted to control viscosities.

Fused Ring Based Imidazolium Ionic Liquids



CO₂ capacities for compounds 1-A through 1-D

Compound	CO ₂ Absorbed (mmol/g)	mmol CO ₂ per mol IL	Weight %
1-A	0.082	0.087	4.436
1-B	0.088	0.040	4.131
1-C	0.403	0.082	4.022
1-D	0.110	0.087	5.341

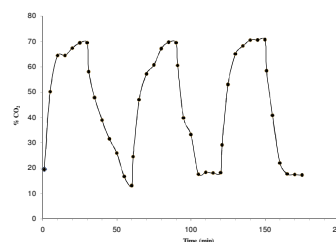
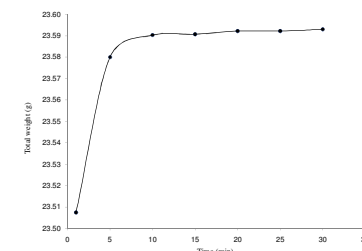
Compound	CO ₂ Absorbed (mmol/g)	mmol CO ₂ per mol IL	Weight %
2-A	0.0702	0.5338	3.732
2-B	0.1331	0.0105	4.366
2-C	0.1386	0.0088	5.647

CO₂ capacities for compounds 2-A, 2-B and 2-C

Compound 1-A	Total Weight (g)	
1	1.007	Final
2	0.507	Initial
3		Diff
4	0.000405	Thru Mass CO ₂ (g)
5	0.000408	% weight CO ₂
6	0.000408	
7	0.793427	After Vac CO ₂ weight
8		
9	0.7941	net CO ₂ at Vac
10	0.7940	net CO ₂ (g) (vac)
11	0.0004	
12		
13	12.7070	Difference (g)
14	12.7062	% max
15	12.8024	
16	12.8154	
17	12.8162	
18	12.8010	
19	12.8028	
20	12.8028	

Representative kinetic data of compound 1-A. CO₂ was bubbled through an equimolar solution of the IL and DBU (superbase) at a rate of approximately 30 ml/min, for 30 minutes.. The weight was measured every 5 minutes. After 30 minutes, a vacuum was pulled on the system to removed any physically dissolved CO₂.

Kinetic plot of compound 2-C for a single sorption cycle of CO₂. While the total capacity of the IL-superbase system was near 110% (mol/mol), maximum chemical absorption was achieved in less than 5 minutes of exposure to CO₂. This shows a 50% increase in uptake rate as compared with Bmim[TF₂N].



Conclusions

- Ionic liquids provide a viable alternative as a medium for CO₂ capture.
- We are able to tune the properties of ILs via systematic additions of electron withdrawing groups tethered directly to the imidazole backbone.
- Preliminary results indicate a lowering of CO₂ desorption temperature and an increase in CO₂ uptake kinetics.
- Further modulation, via addition of novel ancillary chains, should provide a more optimized system overall.